



Short communication

Characteristics of Li_2S_8 -tetraglyme catholyte in a semi-liquid lithium–sulfur batteryMarco Agostini^a, Dong-Ju Lee^b, Bruno Scrosati^c, Yang Kook Sun^{b,d}, Jusef Hassoun^{a,*}^a Department of Chemistry, University of Rome Sapienza, Rome 00185, Italy^b Department of Energy Engineering, Hanyang University, Seoul 133-791, South Korea^c Italian Institute of Technology, Genova, Italy^d Department of Chemistry, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Saudi Arabia

HIGHLIGHTS

- Li_2S_8 –TEGDME catholyte is used in a safe, semi-liquid lithium–sulfur cell.
- The cell is characterized by remarkable safety and non-flammability.
- The 2 V-cell shows a capacity ranging from 430 $\text{mAh g}^{-1}\text{s}$ to 700 $\text{mAh g}^{-1}\text{s}$.
- The cell stability is affected by the voltage cut-off as demonstrated by XPS.
- LiNO_3 -addition to the catholyte stabilizes the cell under extended voltage limits.

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ABSTRACT

In this paper we exploit the use of a Li_2S_8 -containing electrolyte based on a non-flammable TEGDME in a semi-liquid lithium cell, characterized by a configuration usually employed in conventional lithium ion batteries. The cell, using a sulfur-free, Super P carbon electrode shows a capacity varying from 430 $\text{mAh g}^{-1}\text{s}$ to 700 $\text{mAh g}^{-1}\text{s}$. The cycling tests show that the stability of the cell is strongly affected by the voltage cutoff directly controlling the electrochemical process, in particular the polysulfide shuttle reaction. In this respect, XPS measurement shows the deposition of Li_2S_2 salt at the lithium electrode surface as the cell voltage cutoff is enlarged, thus suggesting that the use of the reduced voltage and capacity regimes may lead to higher stability. Under the best control regime, the 2 V cell delivers a capacity of 530 $\text{mAh g}^{-1}\text{s}$, with extremely low polarization and cycling stability extended up to 100 charge–discharge cycles. Furthermore, we demonstrate that enhanced performances may be effectively reached by adding LiNO_3 salt to the electrolyte solution to form a stable, protective SEI film on the lithium surface, thus avoiding the shuttle process and increasing the cell efficiency, even under a full voltage cutoff range, i.e. extending from 1 V to 3 V.

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1. Introduction

The present energy economy based on fossil fuels has led in the last three decades to dramatic increase of greenhouse gases emission resulting in a rise of global warming and temperature, with consequent climate changes and air pollution [1]. In this respect, electrochemical energy storage systems, in particular lithium batteries, proposed as power source for electric vehicles and side

system for renewable energy plants, have triggered great attention [2]. However, the severe targets of the vehicle transportation market [3–6], both in terms of energy density, safety and cost so far required new systems in replacement of the conventional LiCoO_2 /graphite battery [4]. Lithium–sulfur battery, characterized by theoretical energy density of 2600 Wh kg^{-1} , low cost and natural abundance of the active element, appeared as one of the most promising system to meet the market requirements [5]. However, issues such as the dissolution of reaction intermediate, i.e. polysulfide, the volume changes during operation and the poor electronic conductivity with consequent capacity decay and low Coulombic efficiency [7,8], are still preventing the large scale diffusion of the lithium sulfur cell. Several researches, aimed to

* Corresponding author. Department of Chemistry, University of Rome Sapienza, Piazzale Aldo Moro, 5, Rome 00185, Italy.

E-mail address: jusef.hassoun@uniroma1.it (J. Hassoun).

develop stable and efficient electrode material, mainly based on trapping sulfur into inert matrixes, such as carbon and metal oxides, have been so far reported [9–15]. However, the full success of these attempts required the development of suitable electrolyte media, capable to effectively prevent the electrode dissolution, such as that based on dissolved polysulfide acting as physical and electrochemical buffer [16,17]. New, very promising approach is represented by the lithium–sulfur semi-liquid battery in which a polysulfide dissolved in the electrolyte is reduced during cell discharge and oxidized during charge, thus directly acting as liquid electrode [18,19]. Although very interesting, since the liquid nature of the polysulfide prevents problems associated with volume variation, electronic conductivity and electrode dissolution, this approach was so far limited by the deposition of insulating species formed during the process, such as Li_2S_2 and Li_2S , at the cell electrodes, leading to capacity decay upon cell cycling.

In this paper we extended the study originally reported by Cui and coworkers, based on Li_2S_8 liquid cathode in DOL–DME–LiTFSI electrolyte and a glass-type cell with carbon paper electrode [19], to the safe, non-flammable tetraglyme-based electrolyte using the LiCF_3SO_3 salt that is one of the most promising electrolytes for lithium sulfur cell. The electrolyte solvent and the salt play a key role in determining the lithium sulfur battery diffusion, in particular in view of the possible use of the high capacity, lithium metal as the anode of choice. Accordingly, we studied here the TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO₃ catholyte in order to demonstrate its effective suitability for a safe lithium sulfur battery using a conventional cell configuration, typical of the lithium ion battery, characterized by high performances in terms of delivered capacity and cycling stability. We demonstrated that a proper control of the redox process magnitude, i.e. by limiting the lithium–sulfur reaction to species dissolved in the liquid phase, greatly enhances the cell behavior in terms of cycling stability and cell polarization. X-ray Photoelectron Spectroscopy (XPS) evidenced that a large operating voltage window, ranging from 3 V to 1 V vs. Li^+/Li , may lead to the excessive formation of Li_2S_2 specie that is characterized by limited solubility and may precipitate at the lithium electrode surface, thus depressing the lithium–sulfur semi-liquid cell stability. Furthermore, limited cycling voltage range produced very stable capacity extending up to 530 mAh g^{−1}_S at a voltage of 2 V and with extremely limited polarization, thus with no signs of lithium sulfides precipitation. We also proposed a possible way to definitively limit the redox shuttle process, i.e. by excluding the voltage limitation condition and adding a LiNO₃ salt to the TEGDME electrolyte solution which leads to the formation of a stable passivating SEI film on the lithium anode surface. [8,17] This new electrolyte configuration, having the additional bonus of the non-flammability and the limited expected cost, directly prevented the polysulfide shuttle reaction and stabilized the discharge–charge process, with a capacity of 600 mAh g^{−1} as referred to the overall sulfur amount, an efficiency approaching 100% in the 1 V–3 V voltage range and a limited cell polarization. We believe that the study here reported may reveal very important factors aimed to the proper control of the high energy, lithium–sulfur semi-liquid battery.

2. Experimental section

2.1. Catholyte synthesis

The liquid cathode, following named catholyte due to its dual role, i.e. cathode and electrolyte, was prepared following the procedure developed in our laboratories [16]. The catholyte precursor synthesis was performed by adding pieces of lithium metal (Chemetall) and elemental sulfur (Aldrich) in a 2:8 molar ratio, respectively using TEGDME solvent (Aldrich) with a final Li_2S_8 ratio

of 5% w/w. The mixture was heated at 80 °C for 24 h to obtain a red-colored solution in which no residual sulfur or lithium was observed. The final catholyte solution was obtained by adding 1 mol of LiCF_3SO_3 salt to 1 kg of the TEGDME–5%Li₂S₈ solution.

2.2. Carbon electrode and cell design

Carbon material (Super P Timcal, 80% wt) and a polyvinylidene fluoride binder (PVDF, Solef, 20%) were mixed for 3 h in an N-methyl-2-pyrrolidone (NMP, Aldrich) solvent. The resulting slurry was deposited on an aluminum foil by doctor-blade and dried under vacuum at 100 °C for 12 h in order to remove residual solvent, with final carbon loading of 0.8 mg cm^{−2} and 50 μm of thickness. Polypropylene, Swagelok T-type cells were assembled in an argon-filled glovebox (H_2O and O_2 content less than 1 ppm) using lithium foil anode (Chemetall, thickness 200 μm) as a counter-reference electrode, carbon Super P as a working electrode and Whatman glass fiber (soaked by 50 μL of catholyte solution) as a separator. The Li_2S_8 content in the T-cell was of 3.20 mg cm^{−2} while the sulfur content was of 3.03 mg cm^{−2}. The cell specific capacity during cycling was referred to the overall sulfur mass.

2.3. Electrochemical characterization

The lithium–catholyte interface stability was studied by electrochemical impedance spectroscopy applying a 10 mV AC amplitude signal to a Li/catholyte/Li symmetrical cell in a 500 kHz–10 mHz frequency range. The determination of the lithium transference number was obtained by using Bruce & Vincent method [20] consisting in the combination of AC and DC polarization pulses applied to a Li/catholyte/Li symmetrical cell. The applied DC signal was of 20 mV while the AC impedance spectra were performed

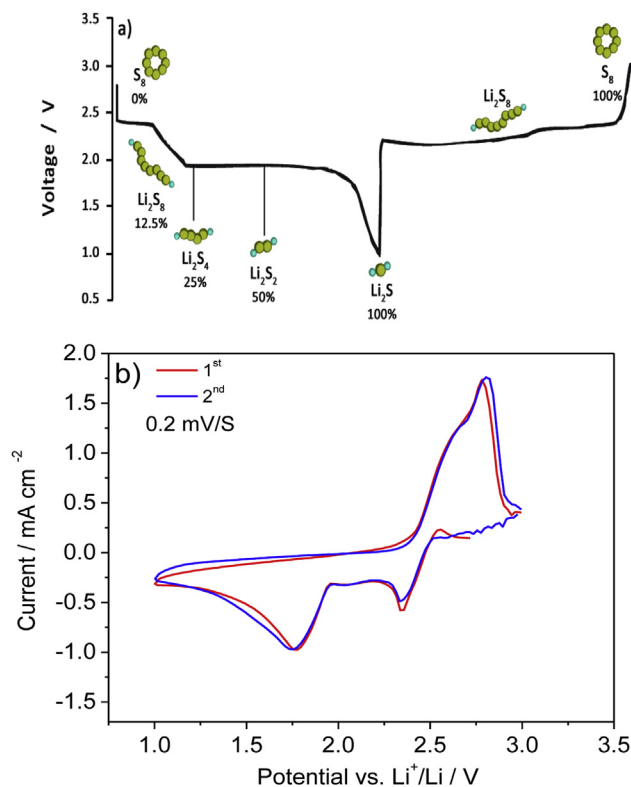


Fig. 1. (a) Reduction–oxidation schematic profile in a Li–S cell with a description of the intermediate polysulfide reaction products. (b) Cyclic voltammetry of a Li/TEGDME–1mLiCF₃SO₃–5%Li₂S₈/SP-carbon cell. Scan rate 0.2 mV s^{−1}, potential limits 1 V–3 V vs. Li^+/Li .

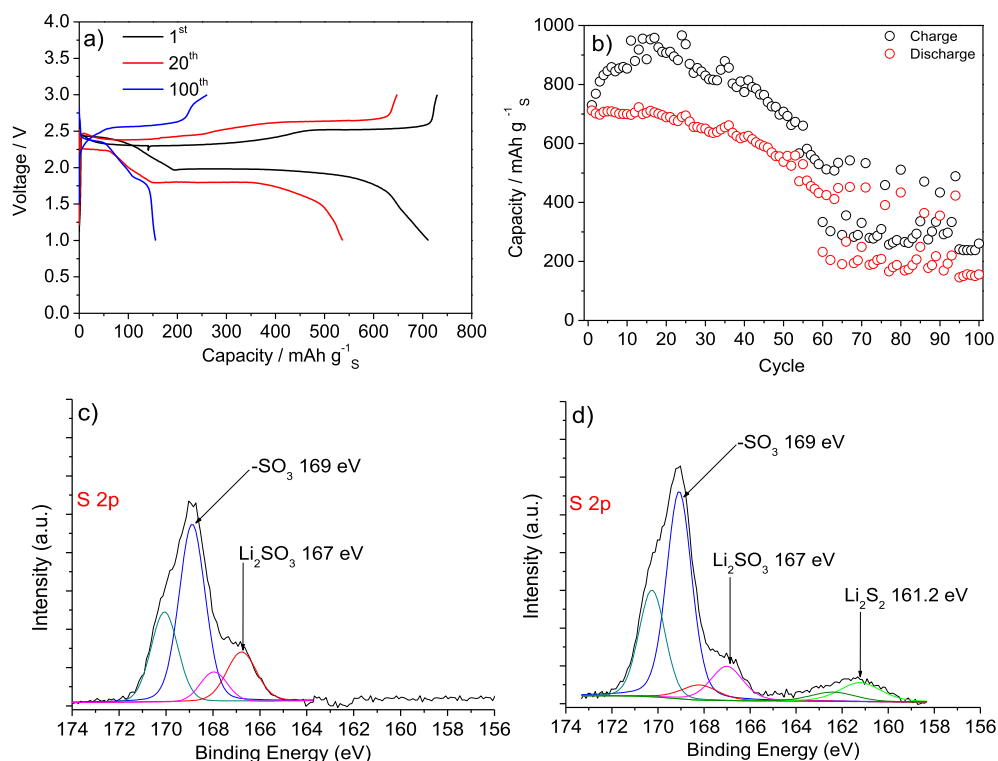


Fig. 2. Voltage profile (a) and cycling behavior (b) of Li/TEGDME-1mLiCF₃SO₃-5%Li₂S₈/SP-carbon cell performed at 25 °C at a current rate of 110 mA g⁻¹_s, within 1 V–3 V voltage limits. (c) XPS S 2p spectra of Li foil soaked into polysulfide-free electrolyte, TEGDME-1mLiCF₃SO₃, for 7 days and (d) XPS S 2p spectra of the Li foil recovered from the Li/TEGDME-1mLiCF₃SO₃-5%Li₂S₈/SP-carbon cell after 50 discharge-charge cycles.

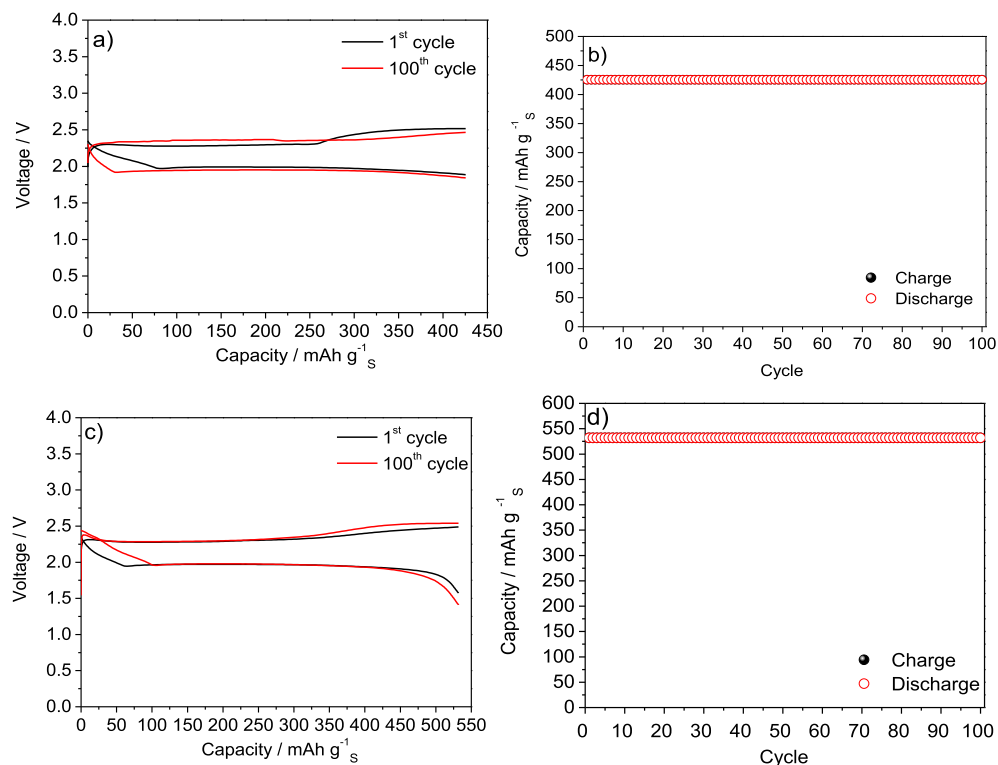


Fig. 3. Voltage profiles (a,c) and cycling behavior (b,d) of Li/TEGDME-1mLiCF₃SO₃-5%Li₂S₈/SP-carbon cell performed at 25 °C by fixing the discharge-charge capacity at 430 mAh g⁻¹_s and 530 mAh g⁻¹_s, respectively. Current rate: 110 mA g⁻¹_s.

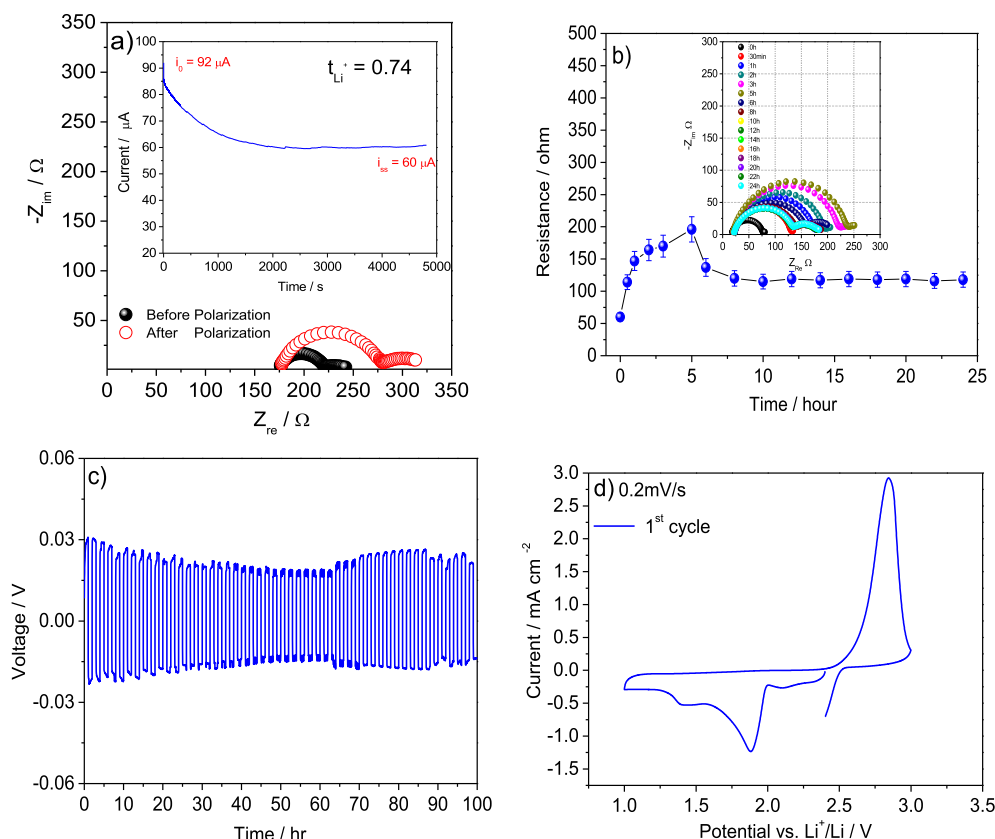


Fig. 4. Electrochemical characteristics of the TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO₃ catholyte. Transference number measurement with impedance response before and after polarization and, in inset, the corresponding current–time evolution following a dc polarization of 20 mV in a Li/TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO₃/Li symmetric cell (a); time evolution of the resistance of the symmetric cell within inset the corresponding Nyquist plots (b); lithium deposition–stripping overvoltage of the symmetric cell cycled at a current of 0.1 mA cm^{−2} (c) and cyclic voltammetry of a Li/TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO₃/SP-carbon cell performed with a scan rate of 0.2 mV s^{−1} vs. Li⁺/Li (d). Temperature: 25 °C.

before and after DC polarization in a frequency range of 500 kHz–10 MHz, using a 10 mV amplitude. All the above tests were performed using a VSP Biologic instrument and a 2032 coin-type cell using a 1.6 cm-diameter (2.01 cm² surface) lithium foil electrodes.

The lithium stripping–deposition test was performed on a Li/catholyte/Li swagelok T-type symmetrical cell galvanostatically cycled using a current of 0.1 mA cm^{−2} applied by a Maccor series instrument. The galvanostatic cycling tests were run on Li/catholyte/SP-carbon swagelok T-type cells within various capacity–voltage limits and a current rate of 110 mA g^{−1} using a Maccor series instrument at 25 °C temperature.

The cyclic voltammetry (CV) test was performed using a three electrode polypropylene T cell, with lithium foil as an anode and counter electrode and carbon Super P as a working electrode. The test was run with a scan rate of 0.2 mV s^{−1}, in the voltage range of 1 V–3 V using a VSP Biologic instrument.

2.4. X-Ray photoelectron spectroscopy

The measurements were carried out with an XPS, JEOL, JPS-9010TR using a focused monochromatized Al K α radiation ($h\nu = 1486.6$ eV). In order to avoid the moisture exposure the samples were directly connected through an argon filled transfer chamber to the XPS spectrometer. The chamber pressure used during the analysis was of 2×10^{-7} mbar and the analyzed sample area had a diameter of 300 μ m. The binding energy scale was calibrated from the hydrocarbon contamination by using the C 1s peak at 285.0 eV. The peak positions and areas were optimized by using Multipack Spectrum ESCA program. Two different samples

were studied. The first, used as blank sample, was a Li foil after aging in the polysulfide free electrolyte for 7 days in order to see the impact of solvent and salt on the lithium surface. The second sample consisted of Li foil recovered from a T cell after 50 charge–discharge cycles in the catholyte aimed to observe the reaction products formation at the surface of the lithium foil.

3. Results and discussions

The lithium–sulfur discharge–charge profile [21], together with the sequence of the reaction products in organic electrolyte, are summarized in Fig. 1a. The scheme of Fig. 1a shows that during the first step of the discharge, in the 2.5 V–2.0 V voltage range, the sulfur is reduced through a sequence of soluble polysulfide ions (S₈^{2−}, S₇^{2−}, S₆^{2−}, S₅^{2−}) to finally form Li₂S₄ [22–24]. The second step, evolving at 2.0 V, corresponds to slow kinetics reaction of Li₂S₄ to form the Li₂S₂, while the last reduction stage, at voltage lower than 2 V, corresponds to the conversion of Li₂S₂ to Li₂S that is hindered by the slow Li₂S diffusion in the electrode bulk [22–24]. Furthermore, cyclic voltammetry in Fig. 1b, performed using the catholyte, lithium and Super P carbon electrode, shows 3 peaks during the cathodic scan, that become merged in one broad peak during the anodic scan, associated with the above mentioned processes [22,23].

Cycling tests in lithium cell using the catholyte solution have been performed using the voltage window extended from 1 V to 3 V vs. Li. This wide voltage range leads to a relatively high capacity, i.e. of the order of 750 mAh g^{−1}, during the first cycles as demonstrated by the cell voltage profile reported in Fig. 2a. However, low

efficiency and capacity decay are observed upon prolonged cycling (see Fig. 2b reporting the evolution of the capacity during the test). The capacity decay and the cell polarization rise, observed by comparing the 1st and the 100th cycles in Fig. 2a, indicate a loss of the active Li_2S_8 polysulfide and an increase of the cell resistance, respectively, thus suggesting the precipitation of the polysulfide active material from the solution to the electrodes, in particular to the lithium anode [25]. With the aim to confirm this aspect, XPS spectra in the S2p region have been performed. Fig. 2c, reporting the XPS blank signal obtained by using a lithium foil aged for 7 days in a bare, Li_2S_8 -free electrolyte, shows two peaks, each split by the effect of the spin-orbit coupling into S 2p_{3/2} and S 2p_{1/2} components separated by 1.18 eV and with an intensity ratio of 2:1 [26]. The main XPS peak in Fig. 2c at 169 eV (blue in the web version curve) is characteristic of the C–SO₃ bonds [27,28] while the second peak at around 167 eV (red in the web version color) may be associated with Li_2SO_3 [29] formed by partial LiCF_3SO_3 degradation during the SEI film formation at the lithium surface [28]. Fig. 2d reports the XPS spectrum of a lithium foil recovered after 50 discharge–charge cycles in a Li/catholyte/SP-carbon cell, within the 1 V–3 V voltage range. This figure evidences the peaks at 169 eV and 167 eV, already observed in the blank sample in Fig. 2c, in addition to new peak centered at 161.2 eV (green in the web version curve) associated with Li_2S_2 [29], thus confirming the above mentioned deposition of the sulfide at the lithium surface during the cell cycling reported in Fig. 2(a, b).

The drawback observed in Fig. 2, i.e. shuttle reaction and consequent cell failure, may be effectively reduced in the semi-liquid cell by decreasing the cycling voltage window and limiting the lithium–sulfur reaction magnitude. Fig. 3, reporting the cell behavior using a capacity limit of 430 mAh g^{−1} (a, b) and 530 mAh g^{−1} (c, d), respectively, evidences a very low polarization and a cycling behavior extended up to 100 cycles. The remarkable stability observed in Fig. 3 is most likely due to a favorable operative condition avoiding the excessive formation of Li_2S_2 and limiting its precipitation from the solution to the electrodes surface, in particular to the lithium anode.

The most suitable solution to avoid the polysulfide shuttle reaction in the TEGDME-based electrolyte may be represented by the addition to the solution of LiNO_3 , i.e. a salt forming a protective SEI film on the lithium surface inhibiting the Li_xS precipitation during the discharge process [17]. Accordingly, a TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO_3 solution was prepared and characterized as reported in Fig. 4, e.g. in terms of lithium transference number (a), stability against lithium metal (b), lithium stripping–deposition polarization (c) and cyclic voltammetry (d). Fig. 4a demonstrates a lithium transference number, measured by following the Bruce–Vincent equation, [20] as high as 0.74 that is a value only slightly lower than that expected for a simple Li_2S_8 –TEGDME–LiCF₃SO₃ system [16], this probably due to the formation of bound ionic couples resulting from the excess of mobile ions produced by the addition of LiNO_3 . The Nyquist plots of Fig. 4b show an initial increase of the lithium–electrolyte interphase resistance from 55 Ω to 180 Ω, most likely due to the SEI film formation, followed by a decrease and stabilization of the resistance at 130 Ω as the SEI film is partially dissolved and finally consolidated. Fig. 4c evidences a stripping–deposition polarization limited to about 20 mV for several cycles, thus confirming the compatibility between the lithium metal anode and the selected electrolyte during the prolonged test. The formation of the polysulfide-shuttle inhibiting film due to the presence of the LiNO_3 additive may be detected by the cyclic voltammetry test reported in Fig. 4d that evidences an extra-peak at about 1.5 V associated with the additive decomposition at the lithium surface with formation of a protective layer, [8] see for comparison Fig. 1b reporting the same test performed using a LiNO_3 -free electrolyte.

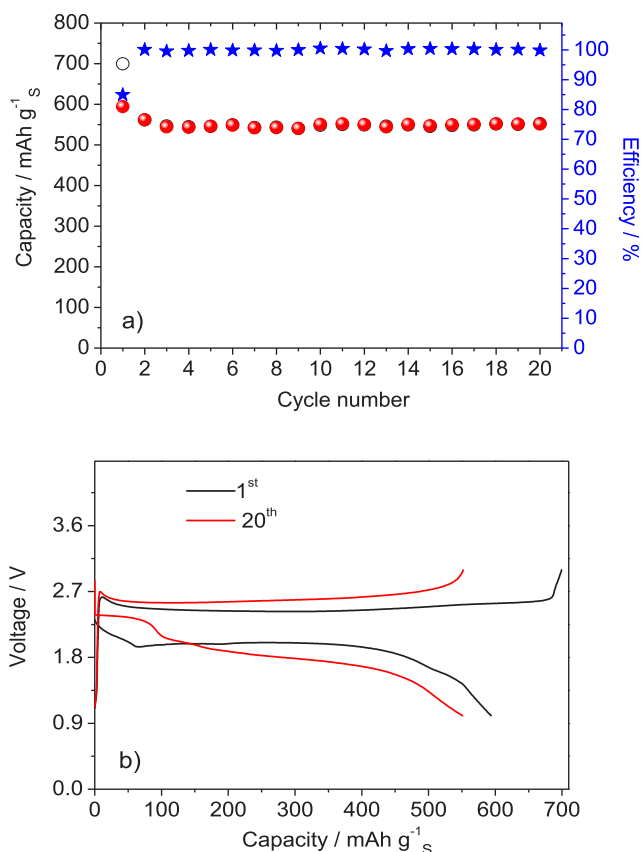


Fig. 5. Cycling response (a) and voltage profile (b) of the galvanostatic test performed on a Li/TEGDME–1mLiCF₃SO₃–5%Li₂S₈, 0.4 M LiNO_3 /SP-carbon cell at 25 °C, using a current rate of 110 mA g^{−1} within 1 V–3 V voltage limits.

The effective role of the LiNO_3 addition in lithium cell was investigated in the full voltage range extending from 1 V to 3 V. The high cycling efficiency evidenced by Fig. 5 confirms the absence of the shuttle reaction over the 20 cycles under study, in particular comparing with Fig. 2b reporting the behavior of the LiNO_3 -free cell. The efficiency increase, associated with the addition of the LiNO_3 shuttle-inhibitor, greatly stabilizes the charge–discharge cycling response that is evolving with a capacity of about 550 mAh g^{−1} (Fig. 5a), however with a slightly increased cell polarization (Fig. 5b) due to the expected additional resistance of the protecting layer.

4. Conclusions

In this paper we reported a lithium–sulfur cell with a semi-liquid configuration using a safe, non-flammable TEGDME solvent. We demonstrated that the proper experimental conditions, in terms of cell voltage cutoff and capacity limit, may preserve the semi-liquid nature of the cell that is characterized by the only presence of dissolved polysulfide acting as the electrochemical active specie with very stable cycling behavior and low cell polarization. The above cell delivered a capacity of 500 mAh g^{−1} over 100 cycles at a working voltage of 2 V, with a theoretical energy density of 1000 Wh kg^{−1}. Furthermore, the tests evidenced that excessive voltage limits resulted in a higher capacity, however with issues on cell cycling stability and polarization, due to the precipitation of Li_2S_2 at the lithium metal surface. This drawback has been strongly mitigated by the use of LiNO_3 additive to the electrolyte solution that effectively prevented the polysulfide shuttle reaction, thus stabilizing the cell cycling and efficiency with resulting capacity of the order of 550 mAh g^{−1} and an average voltage of 1.8 V.

To be notice that the cell here reported was characterized by a lower capacity in respect to the corresponding lithium sulfur cell using a DOL-DME solution as the electrolyte [17]. However, we may remark that the high safety level of the electrolyte solvent here used, i.e. TEGDME, in terms of low reactivity and non-flammability represents a further advantage of our cell, in particular in view of the use of the lithium metal as a high capacity anode material.

Acknowledgments

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